PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 4, 04PITSE06(3pp) (2012)

Phase Composition and Physical Properties of the MnBiCr Films, Obtained by Ion-Plasma Sputtering

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(Received 22 June 2012; published online 23 August 2012)

The paper presents the results of investigations of phase composition and physical properties of the pure Mn, MnCr and MnBiCr films, thickness d ~ 150-550 nm, obtained by a modernized three-electrode ion-plasma sputtering. X-ray analysis and estimation of the size (L) of coherent-scattering regions (CSR) showed that in the pure Mn as-deposited films is formed the nanocrystalline cubic phase of manganese, the size of the CSR which L = 7,4 nm. There is a formation of solid solution nanocrystalline β-Mn phase in the original MnCr films (L ~ 7,5 nm). In the original state MnBiCr films is a mixture of rhombohedral Bi phase (L ~ 10,5 nm) and Mn cubic, which decays by heat treatment at ~ 703 K. Heat treatment of Mn and MnCr films at ~ 773 K leads to the formation of MnO oxide. Analysis of displacement temperature of the initial phase transitions with increasing heating rate in the films allowed for the calculation of the activation energy (Ea) of phase transformations by the Kissinger method. For the MnCr films the activation energy is ~ 3500-4800 K. In the MnBiCr films first phase transition (~ 573 K) is related with melting of Bi, the second, probably due to the collapse of the cubic Mn (~ 653 K, E_a ~ 7000 K). When the film is heated above 673 K and subsequently cooling it, at a temperature of ~ 423 K there is an abrupt increase in resistance of about two-fold. Analysis of the demagnetization curves of the MnBiCr films showed the manifestation of hard magnetic properties in a perpendicular field H_c ~ 16 × 103 A/m.

Study has shown that the addition of Cr in small amounts prevents oxidation of Mn and leads to an increase of the films thermal stability. Thus, the thermostable magnetically hard material in a film form was obtained.

Keywords: MnBiCr Films, Ion-Plasma Sputtering, Magnetically Hard Material, Activation Energy, Coherent-Scattering Region, MnCr Films.

PACS numbers: 64.60.My 64.70.dg 75.70.Cn 81.30.Bx

1. INTRODUCTION

Improvement of magnetic and electrical properties of ferromagnetic alloys, by using various additives, is a perspective task in modern technology. Mn-Bi intermetallic compound is a strong ferromagnetic and produced in large quantities by industrial for obtaining plastic magnets. This magnetic material is sufficiently durable and has a large coercive force. The aim of our work was to obtain this material in the film form and improving the properties of magnetic films obtained by a modernized three-electrode ion-plasma sputtering. The effective cooling rate of films depends on the relaxation time of individual atoms on substrate and its estimated value is 10^{12} - 10^{14} K/s [1]. Thus, we can speak of a "quenching from the vaporous state" (QVS). Feature and advantage of this film is the ability to quickly and cheaply obtaining permanent magnets of all shapes and sizes.

Besides Bi compounds with Mn are also known magnetically hard compounds of bismuth with indium, chromium, and europium. Application of these compounds is limited to special areas of technology due to the difficulties of synthesis, or the high price of the second component. We use the films deposition method which enables the mixing of the Bi and Cr components [2]. Taking into account the full immiscibility of Cr and Bi on the equilibrium phase diagram, Cr refractoriness, and the similarity on the magnetic properties of Mn, Cr was chosen to be added to the MnBi alloy, in order to improve the magnetic characteristics of the material, increasing its corrosion resistance and obstruction of MnO oxide formation.

2. MATERIALS AND METHODS

2.1 Objects of investigations

The objects of investigations were films of pure Mn, MnCr films, the next compounds Mn - (7, 10, 14, 18 at. % Cr) and the ternary system film Mn – 25 at. % Bi – 7 at. % Cr. Film thickness, estimated by weighing the substrates before and after sputtering, are d ~ 150-550 nm. Sputtering was carried out on NaCl single-crystal substrates for the structural investigations by X-ray analysis. The films obtained under identical deposition conditions on the sitall substrate were used to study the thermal stability and physical properties of nonequilibrium structures.

2.2 Methods of investigation

For obtaining the films used the method of ion-plasma sputtering in a vacuum type-setting of targets placed directly on the sputtering surface of the component squares. An additional acceleration of Ar ions impinging on the target and, hence, an increase in the kinetic energy of the atoms depositing onto Sitall (ceramic glass) substrates, was achieved by using a specially designed device in the sputtering setup URM.3.279.014. The acceleration device represents a

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grid of 0.5 mm thick stainless steel plates, isolated from the target table and raised over the surface of sputtered square segments. The plates served simultaneously as a barrier to avoid the horizontal interdeposition of one target metal onto the other. Application of the anode potential to the plates not only prevented them from being sputtered by argon ions, but also produced a considerable additional acceleration of the bombarding ions in the final part of their trajectories just before striking the target surface. Moreover, the atoms sputtered from the target surface also acquired an additional kinetic energy to collide with the substrate. The vapor deposition of the films was carried out under the conditions shown in a Table 1.

The sheet resistance was measured by the four point technique upon continuously heating the film in vacuum 10 mPa. The structure and compositions of the initial and annealed films were studied by the X-ray diffraction patterns obtained with Debye Scherrer camera using the CoKα radiation. The coercive force Hc was measured on a vibration magnetometer in the maximal magnetizing field 0.3 T, attached parallel and athwart surfaces of film.

Calculation of activation energy of the beginning of phase transitions was carried out by Kissinger [4]. Using the method of Kissinger on the temperature dependence of resistivity curves recorded with different heating rates, we can construct the dependence of $\ln(T^2/V)$, from the function F(1000/T). This dependence is satisfactorily described by Arrhenius type. And from the slope of the line we can estimate the activation energy of the beginning of phase transformations.

3. RESULTS AND DISCUSSION

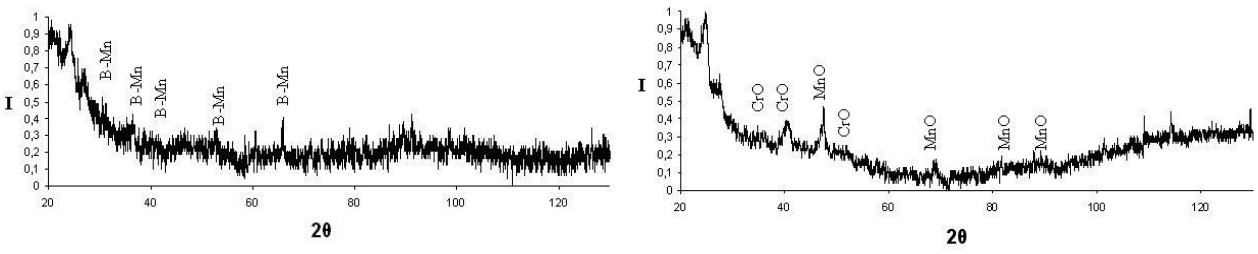
X-ray analysis and estimation of the size (L) of coherent-scattering regions (CSR) showed that in the pure Mn as-deposited films is formed the nanocrystalline β-Mn phase, the size of the CSR which L ~ 7.4 nm and MnO oxide. Heat treatment of pure Mn films in a vacuum at a temperature of 773 K leads to complete oxidation of Mn with the formation of MnO. In the original MnCr films of all compositions formed a solid solution nanocrystalline β-Mn phase, the size of the CSR which L ~ 7,5 nm. As a result of heat treatment at a temperature of 773 K are formed MnO and CrO oxides (Fig. 1). In the original state MnBiCr films is a mixture of rhombohedral Bi phase (L ~ 10,5 nm) and Mn cubic, which decays by heat treatment at a temperature of 703 K. The size of the CSR of Bi rhombohedral virtually unchanged. By comparing the phase composition of the films with low content of Cr and Mn, MnBi films, there is complete disappearance of the MnO oxide in the original state. In MnBiCr films oxides were not found no in the original state or after heat treatment.

Analysis of the displacement onset temperature of phase transformations with heating rate increasing of the films allowed for the calculation of the activation energy of phase transitions (E_A) by the Kissinger method.

For the pure Mn films the activation energy is E_A~5000 K. For the MnCr films the activation energy is in the range E_A ~ 3500-4800 K, depending on film thickness and the Cr content. In studying the temperature dependence of the resistivity of MnBiCr films were observed two phase transitions. The first phase transition (~ 573 K) is associated with melting of Bi. The second phase transition (~ 653 K), presumably associated with collapse of the Mn. The activation energy for the second phase transition is E_A ~ 7000 K.

Table 1 – Conditions of sputter deposited films

	Mn	**Mn – 7 ат.%Cr**	**Mn – 10 ат.%Cr**	**Mn – 14 ат.%Cr**	**Mn – 18 ат.%Cr**	**Mn – 25 ат.%Bi – 7 ат.%Cr**
U, (kV)	2	2	2	2	2	2
I_A, (A)	1	1	2	2	2	1
P_{Ar} (mPa)	120	120	53	53	53	120
t_{dep}, (min)	24	30	36	30	26	26
d, (nm)	160	190	540	320	250	280
η, (pm/s)	110	110	250	180	160	180

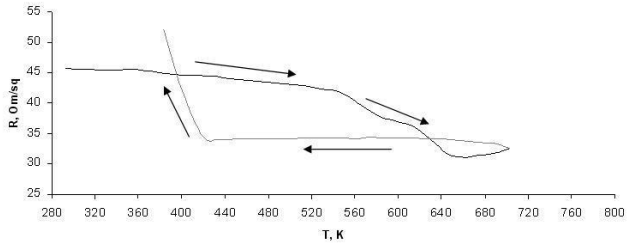


a b

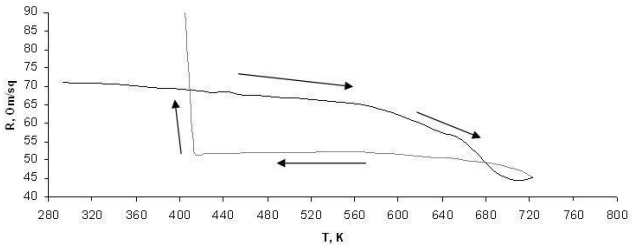
Fig. 1 – X-ray diffraction patterns from MnCr films freshly deposited (a), after heat treatment (b)

Where U is a target voltage; I_A is anode current; P_{Ar} is a pressure of orifice gas (Ar); t_{dep} is a time of sputter deposition; d is a thickness of films; η is a rate of deposition.

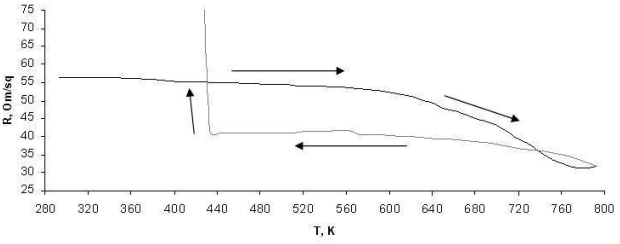
It was also found that after heating the film above 673 K and its subsequent cooling at a temperature of 423 K there is an abrupt increase in resistance of approximately two-fold (Fig. 2 a-c). When the film heated below



a



b



c

Fig. 2 – Temperature variation of resistivity of the MnBiCr film at a heating rate 4,5 К/min (a), 9 К/min (b), 18 К/min (c).

the temperature of ~ 623 K (before the second phase transition) and subsequent cooling, this phenomenon is not observed. Heat treatment at temperatures much higher than the specified limit ~ 923 K also leads to a sharp jump in resistivity at about 423 K. Thus we can conclude a direct relationship of the second phase transition and the observed process. In order to further studying the behavior of the resistivity in the heat-treated films, they were subjected to repeated cycles of heating and cooling (Fig. 3).

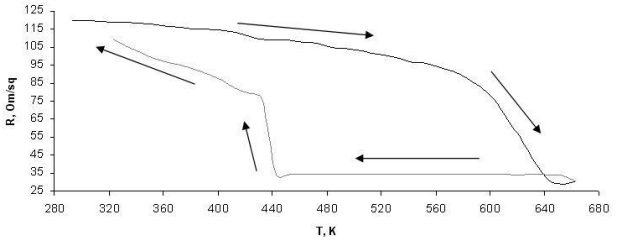


Fig. 3 – Temperature variation of resistivity of the MnBiCr film with repeated heating

As can be seen from the figure, as a result of heating at least the specified temperature and subsequent cooling, there is repeated change in resistance.

The analysis of the demagnetization curves of the films showed the manifestation of the anisotropy of magnetic properties. For the pure Mn and MnCr films coercivity Hc is less than 2.5×10^3 A/m in a parallel field. MnBiCr films showed the value of $H_c \sim 16 \times 10^3$ A/м in a perpendicular field. This indicates that the resulting film is the hard magnetic material.

4. CONCLUSIONS

The effects of Cr additives on the structure of and physical properties of the MnBi ferromagnetic films obtained by the modified method of the three-electrode ion-plasma sputtering were researched by the X-ray analysis, the measuring of relative electrical resistance and magnetometric measuring. As a result, it should be noted that adding the selected components in small quantities to the previously studied MnBi system leads to obstruction of the formation of MnO oxides in the initial state and after heat treatment. Also of note is the high thermal stability of the film, which is manifested in the absence of active oxidation to a temperature ~ 1000 K. We obtain a thermostable and hard magnetic material in the film form. Further studying of magnetic and electrical properties is a perspective task.

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